



UNITED STATES ENVIRONMENTAL PROTECTION AGENCY  
NATIONAL HEALTH & ENVIRONMENTAL EFFECTS  
RESEARCH LABORATORY  
MID-CONTINENT ECOLOGY DIVISION  
6201 CONGDON BOULEVARD, DULUTH, MINNESOTA 55804

OFFICE OF  
RESEARCH AND DEVELOPMENT

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MEMORANDUM

SUBJECT: Responses to questions about toxicity testing at the Ashland Superfund site

FROM: Dave Mount

TO: Darrel Lauren, URS

After receiving a list of questions/issues from you via e-mail (dated September 16), I decided to respond in writing. Compared to a telephone discussion, writing the answers down provides a better means to distribute the discussion to all interested parties. Your original text appears in **bold**, followed by my comments in *italics*.

**UV Light Exposures-** I'm sure you're aware that the UV spectrum and intensity changes throughout the day and seasonally. At another site, Ed Little allowed his equipment to be used to collect actual measurements which were useful but I don't know how they will be reproduced in the lab. *Certainly there are some changes that can occur in the UV spectrum depending on the character of the water column. However, PAHs that can be photoactivated absorb light over a broad wavelength range, particularly when all compounds are considered in aggregate. Likewise, generic UV meters measure a broad range of wavelengths with varying weight across the spectrum. Ed's instruments can provide a wavelength specific spectrum, but you're right, it would be virtually impossible to replicate that exact spectrum experimentally in the laboratory. Moreover, even that spectrum will vary some seasonally. Nonetheless, because of the spread in absorption spectra for different PAHs, I think all this basically just comes out in the wash and in the end you're talking about a +/- 10% kind of uncertainty. There are ways to get around this computationally by calculating "action spectra" for each combination of PAH and UV spectrum (Steve Diamond has a paper out describing this approach), but you'll spend months doing calculations and my bet is you'll come out within spitting distance of where you'll be if you just ignore it, use a UVA-340 lamp and measure total UVA. If you want to do something more rigorous, have at it.*

**I know that organisms do some repair work if they get a night-time regime as well.** *So use a UV photoperiod instead of continuous light. We've used a 14h light:10h dark cycle as an approximation of summer UV exposure - this is a little shorter than the actual sunrise/sunset photoperiod, but assumes that UV penetration into the water column is relatively low close to sunrise/sunset because of the lower total illumination, greater absorption by the atmosphere, and lower incident angle of the sun. Actually the degree of repair during dark periods for damage*

*from PAH photoactivation hasn't been well demonstrated as it has for direct UV damage, but I'll agree it is reasonable to expect that some degree of repair might occur.*

**Most critters are negatively phototactic and hid under stuff like leaf litter (or wood chips), so I think there should be some accounting for this as well, possibly by adding leaf litter to the assay vessels.** *I'll agree that overhead structure such as leaves or macrophytes might provide additional shading where such structures exist, but I'm not ready to say that the assessment of risk should depend on the presence of shading beyond the sediment itself. As such, I think a treatment with sediment but no additional shading material is a must have point of reference. If you think there should be additional treatments in which there is additional shading structure as another point of comparison, there's nothing wrong with that. However, that raises the question of how one decides how to use these two items together in quantifying risk. Unless it can be shown that there is no unshaded habitat at the site, then the unshaded sediment will remain a relevant component of the exposure assessment in my mind.*

**They also hide to avoid being fish food.** *I don't think I'm aware of evidence for predator avoidance by Lumbriculus, Chironomus, or Hyaella beyond their normal activities.*

**I'm also concerned about the larval fish UV tests, in part because I'm used to larvae being around in the spring when phytoplankton blooms provide a lot of DOC and UV absorbance, and in part because I don't think they venture into shallow waters where waves are prevalent. I would also expect turbulence-dependent UV scattering in this area.**

**While there may be UV light measurements in mid lake, the areas of most concern at the site are, I think, either pretty deep and possibly covered with wood chips and similar detritus, or shallow and turbulent.** *That's quite a shotgun blast of issues. I'll start by saying that larval fish tests (with or without UV) weren't my idea, so I'm not going to take full responsibility for defending them. However, I don't find that much compelling in the issues you list. UV absorbance is not a yes/no issue. Yes it is possible that there are differences in spring UV penetration, but it doesn't go away, particularly not in a system as oligotrophic as Lake Superior. In addition, larval fish of various species can be expected to be present over at least a couple months, depending on the spawning times of different species.*

*I don't buy for a second your insinuation that larval fish don't inhabit shallow water – shallow waters are the major nursery areas for most species. Not to go “anecdotal” on you, but as a youth I raised a bunch of fry I caught with a dip net in absolutely open water with an arm's length of the shore right here in front of the lab in Duluth (they turned out to be white suckers, by the way). This argument's a non-starter with me.*

*I don't find the turbulence argument very compelling either. Turbulence might create a small increase in surface reflection (I'd have to consult with experts to find out for sure), but it also increases scattering, which works against your shading argument. If I remember correctly, a large proportion of incident UV is already scattered in the atmosphere, so the incident ray angle for UV is not singularly the angle of direct sunlight. Turbulence could actually increase penetration of low-angle UV rays, since the angle those rays contact the water at will be increased by interacting with a water surface that's no longer parallel with the horizon and might otherwise be reflected. Moreover, Lake Superior experiences many days that are calm with a slick water surface which make this point moot; I have the luxury of getting to see them out of my office window.*

*I also don't know what evidence you have to suggest that larval fish will be sticking to deep water and hiding under wood chips, but if you want to put something forward, we can discuss it.*

**I'm not sure behavioral analyses of confined fish will be transferable to wild fish.** *I'm not sure they would be either. I suggested behavioral observations because I perceived a sense among some stakeholders that direct sediment contact was a major route of exposure for larval fish, and I'm not as sure it is. I thought that perhaps making some behavioral observations during the larval fish exposures might give some clue as to whether the fish actually do stay in contact with the sediment. But if you don't think they'll be useful, don't do them.*

**I also think we should make an extensive effort to collect near-bottom water samples at the site so we know if the lab tests were representative.** *As I understood it, bottom water sampling was already part of the URS plan. My suggestion was to also sample the overlying water in the larval fish exposures to make this very comparison.*

**Sampling-** **I'm sure you recognize that sampling disrupts in situ equilibrium, but I don't know how long it takes to re-establish equilibrium or how to set up tests that account for it.** *Fortunately, cationic metals are not a major concern at this site, which greatly reduces worries about oxic/anoxic layering in the sediment. Sediment desorption studies would suggest that for many organic chemicals, interstitial water comes back in to equilibrium (or maybe pseudo-steady state would be a better term) pretty quickly after it is disturbed. I can tell you that after 24 hours of quiescence in our sediment toxicity tests, a visible oxic/anoxic layering is visually observable. I can't argue that everything is known about re-equilibration rates, but it's a little hard to believe that we're going to re-open this issue at this site when sediment test methods have been standardized to a 24-h equilibration period for as long as they have. However, if you have an alternate proposal, I'm willing to discuss its merits.*

**I was thinking that we might set out SPMDs (or similar) at the site and in lab bioassay duplicates so that we could adjust the pore-water effects concentrations by bioavailability.** *If you want to propose something, I'm willing to discuss it. That said, SPMDs are no panacea either – there are issues of kinetics, biofouling. Plus, I'm not sure how you plan to deploy SPMDs in the field such that it measures chemical activity in interstitial water without also disturbing the sediment.*

**I think it might be very useful to see photographs of the surface and near subsurface as has been done in NY harbor.** *There, they see a very thin yellowish oxidized layer that quickly goes to a black anaerobic layer. It would be important to re-establish such conditions in the lab after the sediments have been disturbed. As I said above, the redox layering will re-establish on its own, at least to some degree. Also, redox condition is much less an issue when the primary issue is PAHs.*

**I really dislike the idea of compositing samples, but I have no reasonable alternative except collecting and running the assays in the same tube and compositing them after the assay to see what concentrations were there.** *If you don't want to composite for toxicity, I'm not sure why you would want to composite for chemistry. Actually, there is some benefit to compositing*

*in that you have much greater assurance that there is coherence between the chemistry and toxicity data.*

**I'm also concerned that pH, NH<sub>3</sub>, and S<sub>2</sub> toxicity could drive the results before re-equilibrium is reached.** *If that happened during equilibration in the lab, then you would expect to happen in the field as well. If you're concerned, measure these parameters in the overlying water. If you find a freshwater sediment that is toxic in a solid phase test (solid phase, not interstitial water tests) because of ammonia, I'd like to get some; we've been looking for one for years to use for method development for TIEs. We've only found one thus far. I don't think this is a worry but, as I said, monitor the overlying water if you're concerned.*

**I see you like centrifuged pore-water but I'm interested to know how 0.1  $\mu$  filters work since this could be done in the field as well as the lab?** *This is not my primary area of expertise. My concerns arise primarily out of our experience that filtered IW often has lower toxicity than centrifuged IW. This doesn't necessarily mean that the PAH concentrations would be different (the observation above wasn't restricted to PAH-contaminated sediments). There are probably people who know more about this than I do. Bob Ozretich of EPA's lab in Newport, OR would probably have an informed opinion, as he has done a lot of PAH analysis in IW.*

**Feeding- Do you feed live prey of tetraamin-like stuff? It seems to me that live food may mean feeding higher in the water column than flakes and that there may be less sediment ingestion in the wild than in aquaria. Daphnid, mosquitoes, or chironomids could be used?** *I don't have experimental data to show it, but suspect that the food uptake route is not a huge issue for PAH exposure of larval fish, because the kinetics of chemical uptake are so rapid for small fish (i.e., the size of larval fatheads). We have unpublished data to suggest that larval fatheads come to steady state with waterborne PAH (fluoranthene, pyrene, and B[a]P) within about 24 hours. This is a little different situation, since food present in the sediment might be equilibrated with a higher PAH concentration (i.e., IW) than the overlying water, but I'd still be surprised if there's much difference. I'm also not sure that larval fish such as fatheads are benthic feeders anyway (not saying they are or aren't). Daphnids (with the exception of newborn Ceriodaphnia or something comparably small), mosquito larvae, or midge larvae, are going to be too large for larval fathead to ingest. We generally use brine shrimp nauplii to feed larval fatheads, but that's not in the context of trying to match a level of contamination in the diet.*

**Coal dust- Is there an isotopic signature of for coal that can be used? I would think that EDAX could provide a metals signature but I don't know how to use the data to calculate a concentration.** *Could well be, but I don't know about it, or how it could be applied in this case.*

**I'm a little confused in your discussion about coal and Koc (page 2 of you re-mail to Weldon). At one point you suggest waiting to see if you get aberrant partitioning (paragraph 2) before proceeding with coal dust analyses, but later you suggest you'll have problems accepting the data if Kow and Koc aren't very similar (paragraph 4)- or is this**

**just a reason to shift to bioaccumulation data? This suggests that bioaccumulation data should displace coal or soot measurements and seems like something we should resolve.**

*The draft work plan said that soot, etc. would be measured on only one sample. I think this is a shot in the dark when you don't yet know what partitioning in the sediment looks like. Further, it may very well be heterogeneous across the site, so even if you find appreciable amounts of soot in a single sample, there's not a good way to extrapolate that across the site. The suggestion to wait until the IW analysis was done was an effort to focus that type of analysis on sites where it was most likely to yield important information.*

*With regard to bioaccumulation testing, my point is that if one or more IW analyses (or soot, coal, or whatever) suggest that bioavailability of PAHs is lower than would be expected from generic Koc calculations, I would not be prepared to support raising remedial goals on that basis unless there was a second line of evidence supporting the assertion that PAH bioavailability is lower than "nominal." A direct measure of biological uptake, like a Lumbriculus test is an excellent way to provide this supporting evidence in my opinion, because it is measured biologically (which is the relevant endpoint, not chemistry) and independently from the other lines of evidence.*

*Absent strong evidence regarding reduced bioavailability, I would be very hesitant to support a site-specific adjustment to literature Koc (i.e., similar to Kow) values for deriving remedial goals. If I were in Xcel's position and I believed reduced bioavailability was an issue at the site, then I would be making a substantial investment in collecting the data needed to make that case convincingly. It is very possible there is a bioavailability issue at the site, but adjusting remedial goals based on that is not a decision to be taken lightly. But that's just my opinion.*

**PAH analyses- You've mentioned HPLC/fluorescence- how good is it at identifying individual PAHs and methylated benzenes? Can it separate photoactivable anthracenes from non-activatable?** *As you probably realize, HPLC/fluorescence does not "identify" compounds, it infers their presence based on retention time and excitation/emission wavelengths. Many people go GC/MS to confirm chemical identities. The advantage of HPLC is the much lower detection limits, and the ability to direct inject water samples (if they aren't too grungy). Having low detection limits is going to be an issue for measuring PAHs in the water column or in the larval fish tests. Just saying "no detect" is useless if the method detection limits are way above the range meaningful for assessing biological effects.*

*I don't know about methylated benzenes. I also don't know what structures you're referring to as photoactivatable and non-activatable anthracenes. Anthracene itself is photo-activatable, and so are the alkyl substituted anthracenes, if one believes QSAR models for photo-activated toxicity (I don't know of any chemical specific data). Maybe I'm missing something here.*

*A final consideration in this area is that HPLC/fluorescence is really effective only for a limited set of compounds, such as the unsubstituted priority pollutant PAHs. Trying to get a solid characterization of most/all substituted PAHs is really beyond the technology and should be done via GC/MS. This brings up an issue that I didn't hear discussed at the meeting in Madison, namely, what is the nature of the site mixture of PAHs with regard to PAH compounds*

*beyond the PP PAHs (e.g., alkyl substitutions)? I don't know what work has been done in this area, but it is important that something be known about that. Doesn't mean every sample must be analyzed for "all" PAHs, but at least some subset should be so that we know the relative amounts of substituted and unsubstituted material in the mix.*